

Fe, Ni and Zn speciation, in airborne particulate matter

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2016 J. Phys.: Conf. Ser. 712 012087

(<http://iopscience.iop.org/1742-6596/712/1/012087>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 46.161.56.104

This content was downloaded on 23/01/2017 at 16:01

Please note that [terms and conditions apply](#).

You may also be interested in:

[Quantitative zinc speciation in soil with XAFS spectroscopy: evaluation of iterative transformation factor analysis](#)

A C Scheinost, A Rossberg, M Marcus et al.

[Lifetime and dissolution kinetics of zinc oxide nanoparticles in aqueous media](#)

Ning Wang, Tiezheng Tong, Minwei Xie et al.

Fe, Ni and Zn speciation in airborne particulate matter

Bridinette Thiodjio Sendja¹, Giuliana Aquilanti¹, Ivano Vassura², Marco Giorgetti²

¹Elettra - Sincrotrone Trieste, Basovizza, Italy

²University of Bologna, Department of Industrial Chemistry, Bologna, Italy

Email: giuliana.aquilanti@elettra.eu

Abstract. The study of elemental speciation in atmospheric particulate matter is important for the assessment of the source of the particle as well for the evaluation of its toxicity. XANES data at Fe, Ni, and Zn K-edges are recorded on a sample of urban dust (from the Rimini area of Emilia Romagna region, Italy) deposited on a filter and on the NIST standard reference material 1648. Using linear combination fitting we give an indication of the chemical species of the three metals present in the samples.

1. Introduction

Atmospheric particulate matter (PM) is a complex mixture of different chemical components which exist as a suspension of solid or liquid particles in air, with a wide dimension range (10 nm to 100 μm). It has been widely demonstrated that there is an association between increased PM concentrations and adverse health effects [1]. Atmospheric aerosol toxicity is connected especially with its chemical composition and its capacity to adsorb toxic substances on the surface. As these particles may be harmful to humans, the assessment of their level and chemical composition are significant from an environmental health perspective. On a global scale, PM is mainly constituted by sulphates, nitrates and ammonium, organic and elemental carbon and in small extent by heavy metals.

Some heavy metals, such as Fe, Co, Zn, Mn, Ni and Cr, are defined essential, since they are present in human beings and they are indispensable, because of their role in some metabolic processes. If these metals are present in the organism at concentrations higher than what is needed for the correct execution of metabolic processes, they provoke toxic effects as well as non-essential heavy metals do. For these reasons, heavy metals emissions in the environment must be controlled. In addition to this, heavy metals are not involved in decomposition processes, and thus they persist in a certain environmental compartment until they are transported in another environmental matrix by a chemical, biological or physical mechanism.

Heavy metals are present in the atmosphere as airborne PM and thus the determination of their concentration in this matrix is fundamental from an environmental health perspective. In addition to the determination, the chemical speciation of such heavy metals, i.e., how the metal is distributed among different chemical states, is fundamental for the understanding of the complex phenomena related to airborne PM. In this context, the use of an elemental specific technique such as the x-ray absorption spectroscopy (XAS) is one of the most suitable synchrotron radiation technique for these studies. In particular the x-ray absorption near edge structure (XANES) part of the spectra can reveal different oxidation and chemical state of a specific metal in the particulate matter and it probes the bulk of a material.

This contribution deals with the XANES analysis of a sample of urban dust (from the Rimini area of Emilia Romagna region, Italy) deposited on a cellulose filter together with the NIST standard



reference material 1648 for comparison. A linear combination fitting allowed us to retrieve information about the chemical speciation of Fe, Ni and Zn present in the sample.

2. Experimental

X-ray absorption near edge structure (XANES) spectra are recorded at the XAFS beamline of Elettra-Sincrotrone Trieste (Basovizza, Italy) [2]. The storage ring is operated at 2.0 GeV in top up mode with a typical current of 310 mA. The data are recorded at the Fe K-edge, Ni K-edge and Zn K-edge. The white beam is monochromatised using a fixed exit monochromator equipped with a pair of Si (111) crystals. Harmonics are rejected by detuning the second crystal. Internal reference of Fe, Ni, and Zn foils are used for energy calibration in each scan. The first inflection points for Fe, Ni and Zn are set at 7112 eV, 8333 eV and 9659 eV respectively.

Two samples have been measured. The first sample referred as 29c3 has been collected in urban area of Rimini in the Emilia Romagna Region on 10 cm diameter quartz membrane by means of an ECHOHiVol TCRTECORa sampler equipped with a PM2.5 sampling head and operating at the flow rate of 200 l/min. The sampled volume is 394.4 m³, and the PM2.5 filter density is 0.502 μg/cm². More information about sample 29c3 is reported in [3]. The second sample is a powder of NIST standard reference material 1648. For the XANES measurements the latter is uniformly distributed on a kapton tape. The XANES spectra are collected in fluorescence mode with the sample positioned at 45° with respect to the beam. The total fluorescence yield is measured as a function of the x-ray energy using a silicon drift detector. More than one spectrum was collected per each sample. The spectra are then averaged and normalized according to the standard procedure using the ATHENA program [4].

3. Results and discussion

Figure 1 shows the normalized XANES spectra at Fe (panel a)), Ni (panel b)) and Zn K-edge (panel c)) of the NIST standard reference material (black line) and of sample 29c3 (red line). For the three edges the data of the samples 29c3 show overall the same features of those of the NIST sample. This indicates that the local environment of the three metals in the 29c3 sample is similar to that in the NIST sample. Nonetheless a few differences can be observed.

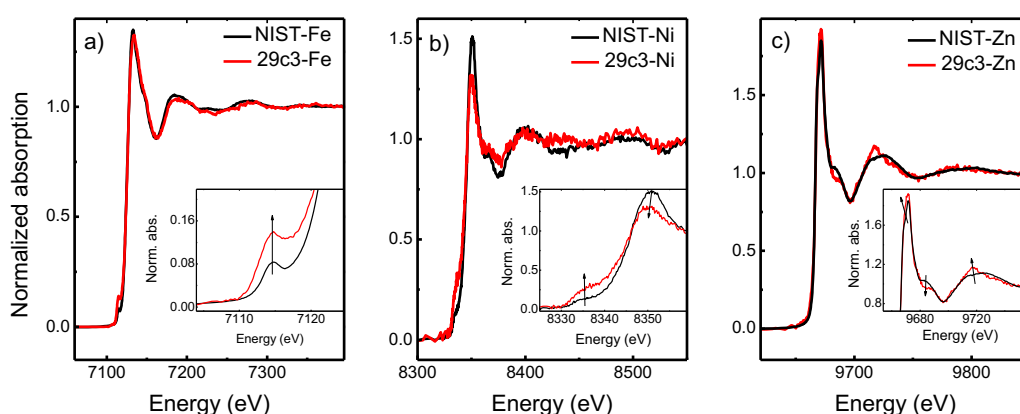


Figure 1. Superimposed x-ray absorption spectra around Fe a), Ni b) and Zn c) K edges for NIST (black line) and 29c3 (red line) samples. The inset highlights the differences between the spectra of the two sample per each edge.

For the iron data the centroids of the pre-peak is at 7114.6(1) for both samples. This indicates that the iron species in the two samples contain predominantly ferric iron [5] and, if a fraction of ferrous iron exists, the Fe²⁺/Fe³⁺ ratio does not vary in a significant way. However, the inset of Fig.1a) shows that the intensity of the pre-peak is higher in the case of the 29c3 sample indicating that an

increased fraction of iron possesses a geometry allowing a higher probability of d-p orbital hybridization, i.e. either a tetrahedral geometry or, at least, an octahedral geometry more distorted than that possessed by iron in the NIST sample [6]. The data at nickel K-edge are affected by a higher noise level because of the low concentration of the Ni species. Nonetheless, there are two remarkable differences between the spectra of the two samples (inset of Fig.2b)). The intensity of the shoulder at 8335 eV increases from the NIST to the 29c3 sample. We observe an opposite behavior for the main resonance at 8351 eV that decreases in intensity from the NIST sample to the 29c3 sample together with a shift to lower energies. The data at Zn K-edge are shown in Fig.1c). The absence of a pre-peak is expected because of the d^{10} electronic configuration of Zn. The spectral features of the two spectra are compatible with zinc in six-fold coordination by oxygen/nitrogen anions.

In order to quantify the chemical species in the samples that are composed by multicomponent mixture we use a linear combination of spectra of various reference samples. The procedure, implemented on ATHENA [4], uses a least-squares algorithm to refine the sum of a given number of reference spectra to an experimental spectrum. The choice of proper reference spectra is critical in such kind of analysis and must be done gathering as much information as possible about the system under study. Figure 2 shows the XANES part of the normalized spectra together with the linear combination fitting curves for the NIST samples at the three edges. The quality of the fit, which can be quantified by the R-factor (reported in Table 1), indicates the proper choice of the reference compounds.

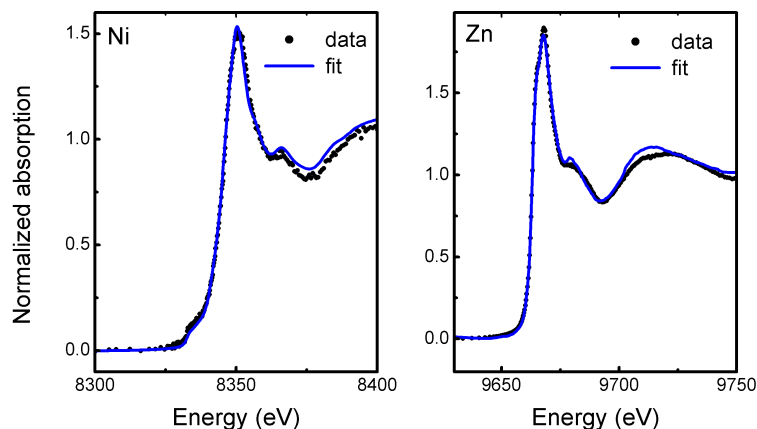


Figure 2. Comparison between the normalized spectra of the NIST sample at Ni and Zn K-edge (black dots) and the linear combination fit (blue line).

Table 1 summarizes the results obtained for Ni and Zn by using linear combination fitting method through Athena package.

Table 1. Relative amounts of the different chemical species obtained using linear combination fitting for Ni and Zn species.

Ni K-edge				
	<i>Ni metal</i>	<i>NiSO₄·6H₂O</i>	<i>NiFe₂O₄</i>	<i>R factor</i>
<i>NIST</i>	0.25(1)	0.33(2)	0.45(3)	0.0024
<i>29c3</i>	0.63(2)	0.19(2)	0.23(3)	0.0024
Zn K-edge				
	<i>ZnCO₃</i>	<i>ZnSO₄·7H₂O</i>	<i>Zn(NO₃)₂</i>	<i>R factor</i>

NIST	0.20(1)	0.39(3)	0.48(3)	0.0012
29c3	0.11(3)	0.09(8)	0.8(1)	0.0092

For iron K-edge, we consider the same species reported in [7], as well as $\text{Fe(II)SO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{Fe}_2(\text{III})(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$ without obtaining a satisfactory fit for NIST nor for 29c3 sample. This indicates the presence of a different Fe containing compound for which no reference spectra are available.

For the data at Ni K-edge the chemical species are compatible with what is reported in [8]. The presence of metallic nickel is not reported though. However, the shoulder at 8335 eV highlighted in the inset of Fig. 1b) can be reproduced only if the spectrum of metallic nickel is used in the linear combination fit. The fitting procedure indicates that the fraction of metallic Ni increases significantly from 25% to 63% from the NIST sample to the 29c3 sample.

For Zn K-edge we use the three reference spectra according to [9]. The quality of the linear combination fitting decreases from the NIST sample to the 29c3 indicating that the choice of the reference spectra is not ideal and probably some components are missing. However in both samples the local environment is compatible with a Zn coordination of 6 O/N atoms.

To conclude, we perform a preliminary XANES study at Fe, Ni and Zn K-edges of the NIST reference sample 1648 and of an airborne PM sample deposited on a cellulose filter to get information on the chemical species present. This is important for the assessment of the health effects of aerosols. In fact these depend not only on the size distribution, but also on the chemical composition of the particles. In addition, knowledge on the chemical speciation of metals in PM is able to shed some light on the specific sources (natural, anthropogenic) of the metals in different chemical forms.

Acknowledgements

B. Thiodjio Sendja acknowledges the Training and Research in Italian Laboratories (TRIL) of the International Center for Theoretical Physics (ICTP) (Trieste, Italy) for providing financial support and Elettra – Sincrotrone Trieste (Basovizza, Trieste, Italy) for training on XAFS experiments.

References

- [1] Wiseman C L S and Zereini F 2009 *Science of the Total Environment* 407 2493-2500
- [2] Di Cicco A, Aquilanti G, Minicucci M, Principi E, Novello N, Cognigni A and Olivi L 2009 *J Phys: Conf. Series* 190 012043
- [3] Venturini E, Vassura I, Raffo S, Ferroni L, Bernardi L and Passarini F 2014 *Environmental Science and Pollution Research* 21 11634-11648
- [4] Ravel B and Newville M 2005 *J. of Synchr. Rad.* 12 537-541
- [5] Wilke M, Farges F, Petit P E and Brown G E 2001 *Am.Min.* 86 714-730
- [6] Westre T E, Kennepohl P, de Witt J, Hedman B, Hodgson K O and Solomon E I 1997 *J Am Chem Soc* 119 6297
- [7] Bardelli F, Cattaruzza E, Gonnella F, Rampazzo G and Valotto G 2009 *J Phys: Conf. Series* 190 012192
- [8] Tirez K, Silversmith G, Vincze L, Servaes K, Vanhoof C, Mertens M, Bleux N and Berghmans B 2011 *J Anal At Spectrom* 26 517-527
- [9] Osán J, Meirer F, Groma V, Török S, Ingerle D, Strelci C and Pepponi G 2010 *Spectrochimica Acta Part B* 65 1008-1013